Effect of plastic deformation upon f-centers in alkali halides

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EFFECT OF PLASTIC DEFORMATION UPON F-CENTERS IN ALKALI HALIDES*

By Ryo Kiyama and Fumio Okamoto

Introduction

On the basis of the assumption that vacant lattice sites are generated during plastic flow[1] it is expected that plastic flow will affect the absorption spectrum of a crystal containing color centers. Smekal[2] and Schroeder[3] have found that the F-centers in alkali halide crystals darkened by ionizing radiation are bleached by plastic flow. Jacobs[4] has demonstrated that the bleaching of F-centers does not occur when the additively colored crystals are deformed by uniaxial strain at room temperature. We have found in electrolytically colored crystals that the blue color of a KI crystal containing F-centers bleaches during plastic flow and the yellow color of a NaCl crystal containing F-centers changes very rapidly to blue by irradiating with white light after plastic deformation, whereas the undeformed crystals maintain their coloration for a long time. Now the effect of plastic deformation upon electrolytically produced F-centers in NaCl, KCl, KBr and KI crystals has been investigated in detail by measuring the absorption spectra. The plastic deformation was carried out by die-casting with a pressure of 5,000 kg/cm^2 at room temperature.

Experimentals

Preparation of samples The crystal pieces used in this work were cleaved from large single-crystal blocks synthesized in this laboratory. F-centers were produced in the respective crystals by means of electrolysis with a pointed cathode of nichrome and a flat anode of graphite in the furnace of 600°C and then rapidly quenched. The samples suitable for measurement were cleaved from the inner region of colored crystal.

Procedure The pressure apparatus is shown in Fig. 1. The pressure vessel A is a cylinder with a 6 mm hole having closely fitted two pistons B. The colored crystal

* *This investigation has been done by F. Okamoto, being in the postgraduate course, under the direction of Prof. R. Kiyama.*

1) F. Seitz, *Phys. Rev.*, 80, 239 (1950)
2) A. Smekal, *Z. Physik*, 55, 289 (1929)
3) H. J. Schroeder, *Z. Physik*, 76, 608 (1932)
4) I. S. Jacobs, *Phys. Rev.*, 93, 993 (1954)

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cleaved to a square plate of about 4×4×2mm was set in the sample region C, and deformed to a thin disk of 6mm in diameter by gradually compressing up to 5,000kg/cm² with pistons in the dark at room temperature, and then the deformed crystal was removed from the vessel and mounted on a metal holder for absorption measurements by means of the Beckman Model D U Spectrophotometer.

The absorption spectra of the deformed colored crystals were measured, over the wavelength range from 350 to 1100mμ at room temperature, on each step of the successive treatments as follows: (i) immediately after plastic deformation, (ii) after preservation in the dark and (iii) after irradiation with white light by using 100 watt ordinary incandescent lamp situated apart at a distance of 20cm from the crystal. In these absorption measurements, the deformed uncolored crystals were used as blank crystal.

In auxiliary experiments, the effect of preservation and irradiation upon undeformed colored crystals was examined for comparison with that upon deformed colored crystals.

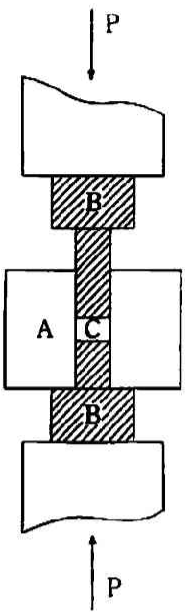

Fig. 1
Diagram of the pressure apparatus
A : pressure vessel
B : pistons
C : sample region

Results

NaCl crystal containing F-centers was deformed in the dark and the deformed crystal was preserved in the dark for 20 hours. The bleaching of the F-band was negligible and there was no detectable growth of long wavelength bands (curves 2 and 3 in Fig. 2). This crystal being irradiated with white light, the F-band was rapidly bleached and the long wavelength bands were developed (curves 4 and 5). By about six hours irradiation, the F-band was almost bleached and the long wavelength bands were enhanced (curve 6).

KCl crystal containing F-centers was deformed in the dark. The bleaching of the F-band was negligible and there was no detectable growth of long wavelength bands (curve 2 in Fig. 3). This crystal being preserved in the dark for 21 hours, the F-band was slightly bleached and the long wavelength bands were developed (curve 3). These changes were markedly accelerated by irradiating with white light (curves 4 and 5). By about six hours irradiation, the F-band was almost bleached and the long wavelength bands were enhanced (curve 6).

KBr crystal containing F-centers was deformed in the dark. The F-band was considerably bleached and the long wavelength bands were developed (curve 2 in Fig. 4). These changes still continued during preservation in the dark (curve 3), and were markedly accelerated by irradiating with white light (curve 4). However, both F- and

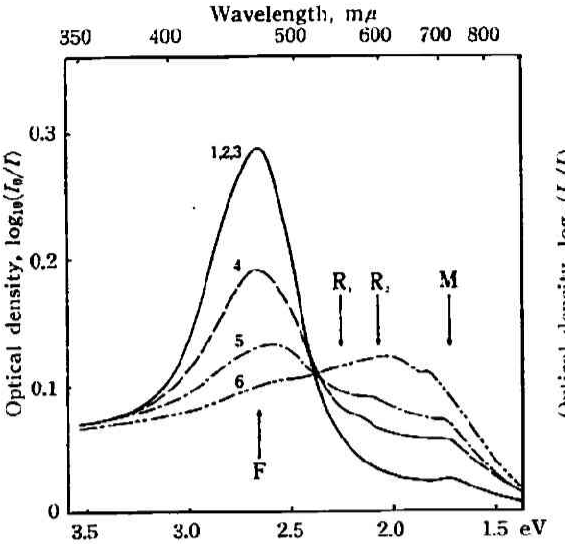

Fig. 2 Changes of the absorption spectrum of F-centers in NaCl crystal after plastic deformation
Crystal thickness=0.82 mm

curve 1 : absorption spectrum of the crystal previous to plastic deformation
2 : immediately after plastic deformation in the dark
3 : after 20 hours preservation in the dark
4 : after 10 minutes irradiation with white light
5 : after further 30 minutes irradiation
6 : after further 6 hours irradiation

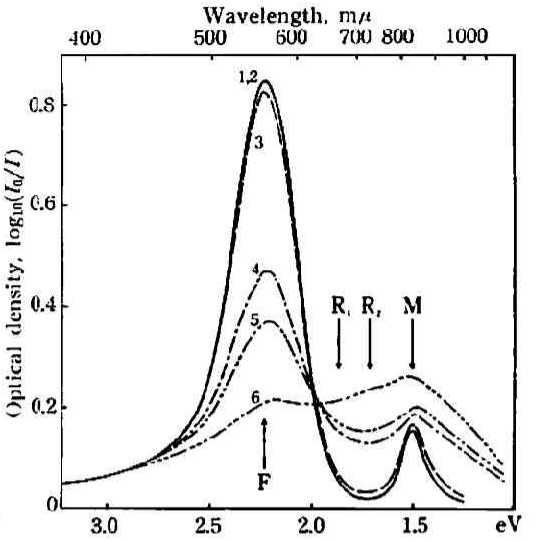

Fig. 3 Changes of the absorption spectrum of F-centers in KCl crystal after plastic deformation
Crystal thickness=1.11 mm

curve 1 : absorption spectrum of the crystal previous to plastic deformation
2 : immediately after plastic deformation in the dark
3 : after 21 hours preservation in the dark
4 : after 10 minutes irradiation with white light
5 : after further 20 minutes irradiation
6 : after further 6 hours irradiation

long wavelength bands were considerably bleached by irradiating for a long time (curves 5 and 6).

KI crystal containing F-centers was deformed in the dark. The F-band was considerably bleached and the weak absorption band was formed at about 520 mμ (curve 2 in Fig. 5). These two bands in the deformed crystal were unstable in the dark at room temperature (curve 3), and were almost completely bleached after 20 hours (curve 4). In this case the irradiation experiment was not performed because the deformed crystal showed rapid spontaneous bleaching in the dark.

Summary

The F-centers in NaCl and KCl crystals are scarcely bleached by the treatment of plastic deformation but those in KBr and KI crystals are considerably bleached, and further the F-centers in deformed KCl, KBr and KI crystals except NaCl crystal are spontaneously bleached during preservation in the dark at room temperature, whereas those in the undeformed crystals are stable for a long time. From this result it is revealed that the rate of spontaneous bleaching in the deformed crystals increases in the

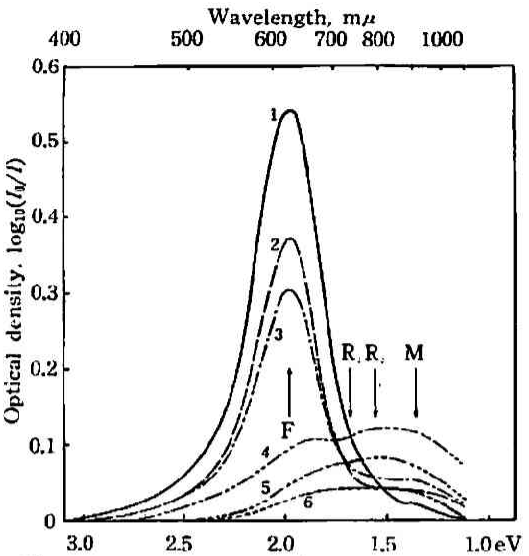

Fig. 4 Changes of the absorption spectrum of F-centers in KBr crystal after plastic deformation Crystal thickness=0.91 mm

curve 1 : absorption spectrum of the crystal previous to plastic deformation
2 : immediately after plastic deformation in the dark
3 : after 22 hours preservation in the dark.
4 : after 30 minutes irradiation with white light
5 : after further 2 hours irradiation
6 : after further 4 hours irradiation

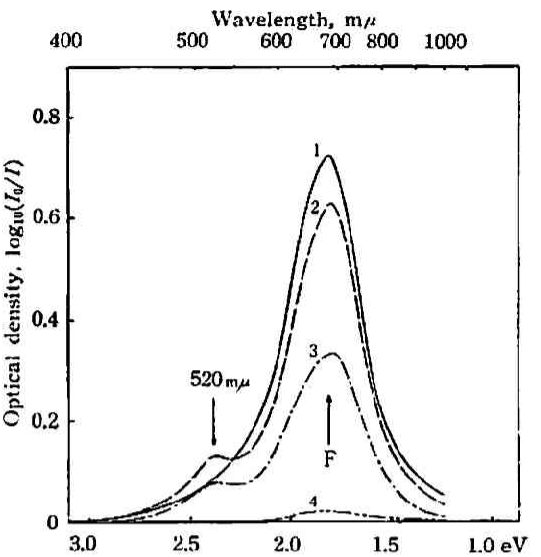

Fig. 5 Changes of the absorption spectrum of F-centers in KI crystal after plastic deformation Crystal thickness=1.03 mm

curve 1 : absorption spectrum of the crystal previous to plastic deformation
2 : immediately after plastic deformation in the dark
3 : after 1 hour preservation in the dark
4 : after further 20 hours preservation

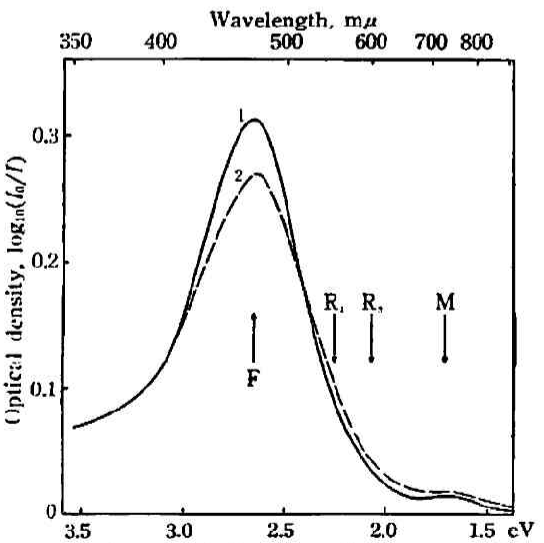

Fig. 6 Change of the absorption spectrum of F-centers in undeformed NaCl crystal by irradiation with white light Crystal thickness=0.82 mm

curve 1 : absorption spectrum of the crystal previous to irradiation
2 : after 4 hours irradiation with white light

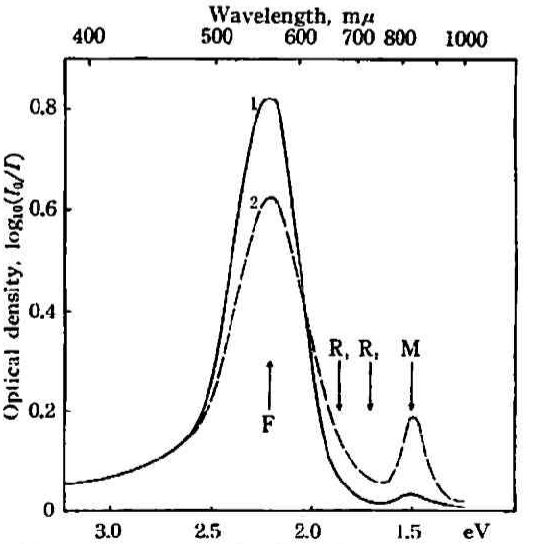

Fig. 7 Change of the absorption spectrum of F-centers in undeformed KCl crystal by irradiation with white light Crystal thickness=1.11 mm

curve 1 : absorption spectrum of the crystal previous to irradiation
2 : after 4 hours irradiation with white light

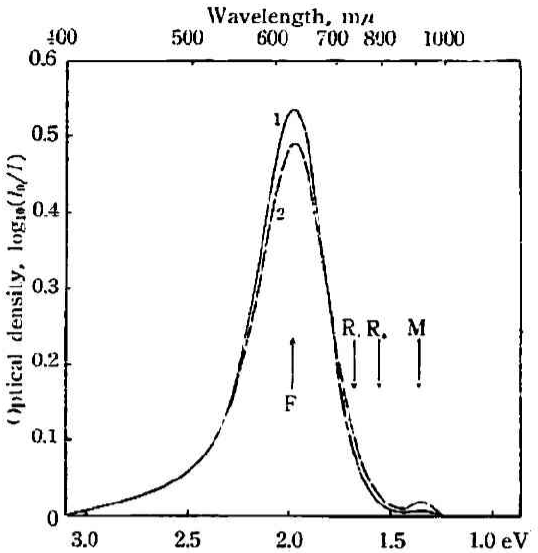

Fig. 8 Change of the absorption spectrum of F-centers in undeformed KBr crystal by irradiation with white light
Crystal thickness=0.91 mm
curve 1 : absorption spectrum of the crystal previous to irradiation
2 : after 4 hours irradiation with white light

order : NaCl < KCl < KBr < KI. Moreover, when the deformed crystals are irradiated with white light, the bleaching of the F-band and the enhancement of the long wavelength bands which may be probably the R_1-, R_2- and M-bands, are more rapid than those in the undeformed crystals (curves 2 in Figs. 6, 7 and 8). This result can probably be ascribed to the large density of clusters of positive- and negative-ion vacancies which are formed during plastic flow[1,5]. For reference the positions of the R_1-, R_2- and M-bands are noted with arrows in each figure.

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5) F. Seitz, *Rev. Mod. Phys.*, 26, 25 (1954)